Degradation of Cibacron Red Dye using ZnO as a Catalyst Coated on the Surface of the Glass in the Photocatalytic Process

A. Sumartono[1*] and W. Andayani
Center for Application of Isotope and Radiation, National Nuclear Energy Agency
Jl. Cinere Pasar Jumat PO BOX 7002 JKSKL Jakarta 12070, Indonesia

ARTICLE INFO

Article history:
Received 20 November 2010
Received in Revised form 27 October 2011
Accepted 04 November 2011

Keywords:
Cibacron-red
Photocatalytic
ZnO

ABSTRACT

Industrial discharges are the main causes of surface and groundwater contamination. Photocatalytic process is one of the methods that could be used to degrade organic compounds that released from industrial wastewater. Photocatalytic process of 10 ppm cibacron red dye with irradiation of UV lamp and ZnO as a catalyst that coated on the surface of the glass the size of 8 cm x 8 cm x 0.4 cm have been studied. Experiments consisting of (i) variation of ZnO catalyst at temperature 200^{o}C, 300^{o}C, 400^{o}C, and 500^{o}C, and (ii) the efficiency achieved by the resulting ZnO obtained from the best variation in (i) as the UV-photocatalytic agent in degradation of cibacron red dye. The UV irradiation was done at interval time 0; 0.5; 1; 2; ; 4; and 6 hours. Degradation could be achieved using ZnO catalyst at temperature 500^{o}C, the percentage degradation at 289 nm, 515 nm, and 545 nm were 84.5±1.0%, 100% and 100%, respectively.

INTRODUCTION

Textile industry is one of the largest water consumer, which produces wastewater containing highly colored effluents, therefore it would affect badly to both surface water and ground water. The presence of large quantities of colored wastewater blocked the penetration of light into the water and subsequently cause imbalance in their ecosystem. In general, the wastewater released from that industry is toxic and biological resistant and would pollute the environment, especially the water resources [1-2].

Decoloration of textile wastewater by conventional chemical and biological methods are difficult. Photocatalytic oxidation of organic substance from wastewater can be used as an alternative method [3]. The use of semiconductor can be activated by sunlight therefore reducing significantly the electric power requirement and operating cost, and the photocatalytic process is its mild operating conditions [4].

Photocatalytic oxidation using a semiconductor such as TiO_2, ZnO, CdS, WO_3 etc. as photocatalyst is one of the various advanced oxidation processes in recent years. They are very promising for effluent treatment mainly due to their high efficiency and simplicity of operation. Combination of UV light with catalysts such as ZnO is one of the advanced oxidation processes. ZnO appears to be suitable alternative to TiO_2, since its photodegradation mechanism has been proven to be similar to TiO_2 [5]. Zinc oxide with the wide bandgap of 3.32 eV as compared to TiO_2 (3,0 eV) is an n-type semiconductor with many attractive features and is capable to generate hydroyl radicals [6].

The photocatalysis with ZnO represents a perspective field, because ZnO can be more efficient than of TiO_2 in the photocatalytic degradation of some dyes in aqueous solution [7-8]. According to Yeber *et al.* [9], ZnO gained much attention in the degradation and complete mineralization of environmental pollutants. ZnO thin film have been found to decompose aqueous solutions of reactive dyes [7,10]. The preparation of film catalyst makes it possible and extend the industrial applications [11]. The sol-gel process and the utilization of dip coating technique are two of the versatile strategies to prepare thin films of particles. ZnO thin film are prepared by different techniques such as metal organic vapour deposition thermal evaporation, oxidation and anodization [12-17].

* Corresponding author.
E-mail address: agustnsmt@batan.go.id

Recently it has been demonstrated that semi conductor materials mediated photocatalytic oxidation of organic compounds is a successful, convention alternative to conventional methods for the removal of organic pollutants from water. The greatest advantage of ZnO is that absorb large fraction of solar spectrum and more light quanta than TiO_2 [18]. Photocatalysis process has been applied to solve various pollutant organic i.e humic acid, dyes, pentachlorophenol, and alkylbenzene sulfonat [19-21].

In this paper we demonstrated preparation of thin films of ZnO catalyst on glass substrates by the sol-gel method using dip coating technique. The films are prepared on glass substrate by dip coating several times and annealed at various temperature i.e 200°C, 300°C, 400°C and 500°C. Further, studies on photocatalytic degradation of cibacron red dye in water using ZnO as catalyst in the various temperature and efficiency of the catalyst was observed. The objectives of the experiment is to find out the temperature influence of formation ZnO on the glass surface and the activity of ZnO as a catalyst to degrade cibacron red dye.

EXPERIMENTAL METHODS

Reagents and equipments

The reagents used in this study were $Zn(CH_3COO)_2$, ethanol, methanol, and acetone. The dye used in this experiment was cibacron red and has a molecule structure in Fig. 1. Reaction vessel is a made of Pyrex glass (Fig. 2) with the size of 25 cm × 11 cm × 7 cm. The reaction vessel is equipped with two 10 Watt UV-light-lamps, magnetic bar and two pieces of glass immobilised with ZnO with size of 8 cm × 8 cm × 0.4 cm.

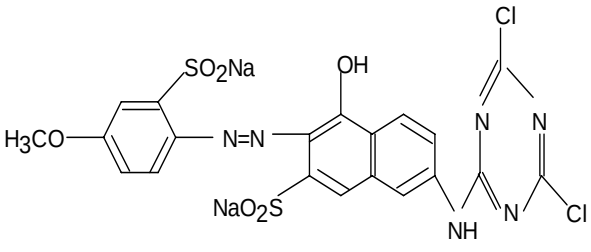

Fig. 1. Molecule structure of cibacron red.

Experimental design

Preparation of ZnO catalyst

Two pieces of glass plates with size of 8 cm × 8 cm × 0.4 cm were soaked in chromic acid, followed by rinsed with water, and acetone. The glass plates were dried in the oven at 110°C for 1 hour, after being cooled were weighed (Wo). The glass plates were coated with 10 ml of Zn asetat at concentration of 1 mg/mL using metanol:etanol (1:4) as a solvent. The coating was done several times on the a surface of the glass. The glass plates were dried in a room temperature, after that were heated at various temperature i.e. 200°C, 300°C, 400°C and 500°C, respectively. After being cooled the glass were weighed (W_1). A 200 ml of 10 ppm cibacron red solutions were placed into the reaction vessel. Irradiation was done at interval time 0; 0.5; 1; 2; 4; and 6 hours using variation of ZnO catalyst processed at different temperature. During irradiation, solution was stirred using magnetic bar. The whole irradiation was done at ambient condition. The change of the spectrum, were analyzed before and after irradiation. The absorption band was measured with a HP 8453 spectrophotometer UV-VIS. After irradiation the catalysts were dried and heated in the oven at 110°C for 1 hour and after cooled were weighed (W_2). From this step, the best condition of ZnO catalyst was used to do the next experiment.

Reusage of ZnO catalyst

The best condition of ZnO catalyst that come from the above experiment was heated in the oven at 110°C for 1 hour. After that,the ZnO catalyst was used again for photocatalytic process up to four times.

Radiation of cibacron red at different treatment

Radiation using the best ZnO catalyst was done at 6 hours at various treatment namely ie ; (a). ZnO+UV light, (b). ZnO, and (c). UV light. After the treatment, the change of the spectrum was measured using spectrophotometer UV-VIS.

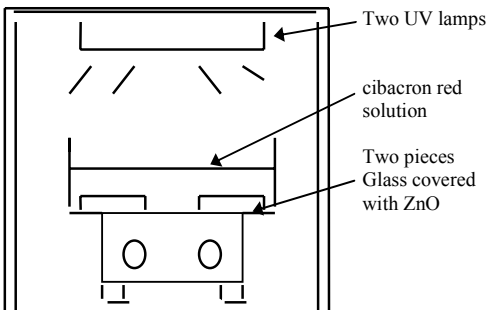

Fig. 2. Reactor for irradiated the sample.

RESULTS AND DISCUSSION

Preparation of ZnO catalyst at various temperature

The weight of the catalyst (W1) at various temperature can be seen in Table 1. It could be seen that the weight of the catalyst on the surface of the glass at high temperature (500^{o}C) more heavy than that at low temperature. At low temperature, the formation of ZnO catalyst only a few, due to the unfinished formation of ZnO. The formation of black thin layer on the surface of the glass indicated that formation of ZnO not complete yet. Therefore, the weight of the catalyst at low temperature less heavy. On the other hand the formation of white thin layer were formed on the surface of the glass when heated at high temperature (500^{o}C). The white thin layer on the surface of the glass indicated that formation of ZnO were completely formed. Heating process was done in order to form ZnO which can be attached on the surface of the glass. The higher the temperature the higher the amount of catalyst were formed.

Table 1. The weighed of catalyst on the surface of the glass at various temperature.

Temperature	Weighed of catalyst (mg)		
	Glass plate 1	Glass plate 2	Total
200^{o}C	1.4	1.4	2.8
300^{o}C	1.6	1.7	3.3
400^{o}C	1.8	1.8	3.6
500^{o}C	2.0	2.0	4.0

The change of Cibacron Red spectra

The cibacron red shows a clear absorption at 289, 515 and 545 nm in the UV and visible region as shown in Fig. 5. The former spectra can be assigned to their substituted aromatic rings, the second and the third are assigned to the conjugated system of the dye molecules. The absorbance of cibacron red after photocatalytic process using catalyst at various temperature i.e. 200^o, 300^o, 400^o, and 500^{o}C, are shown in Fig. 5-8, respectively.

The absorption spectra of cibacron red at 289, 515, and 545 nm using catalyst at 200^{o}C and 300^{o}C decreased slowly after six hour irradiation. At 400^{o}C the intensity spectra at 289, 515 and 545 nm decreased markedly after six hour irradiation using catalyst from 0.278, 0.170 and 0.189 to 0.099 (64.4%), 0.049 (72.5%), and 0.051 (73.2%), respectively. The absorbance values of cibacron red before and after six hours irradiation times are tabulated in Table 2. The percentage of absorbance decreasing after six hours irradiation are tabulated in Table 3. At 500^{o}C, the absorption of cibacron red at 289, 515, and 545 nm after six hours irradiation decreased markedly especially in the visible spectra, its disappeared almost completely, resulting the change of the colour from red into colourless. The changes would suggest destruction of the chromophoric group in the dye molecules. The absorbance in the uv spectra decreased from 0.278 to 0.043 (84.5%), the decrease in intensity is due to the destruction of the aromatic rings in the dye molecules by the attack of OH radicals that formed from phorocatalytic process. The mechanisms degradation of the cibacron red dye is as follows [22] :

$$R_1N{=}NR_2 \xrightarrow{hv} R_1NH_2 + R_2NH_2 \quad (1)$$

$$R_1N{=}NR_2 \xrightarrow{hv} R^{\bullet} + \text{fragmen} \quad (2)$$

$$R^{\bullet} \xrightarrow{hv} \text{product} \quad (3)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet -} \quad (4)$$

$$R^{\bullet +} R^{\bullet} \longrightarrow R{-}R \quad (5)$$

Intermediate product will absorbed foton and will formed product as shown in equation (3). When oxygen was bubbled into the solution, the intermediate product will oxidized into further compound as shown in equation (4). When there is no oxygen bubbled into the solution the organic radicals will combine into oligomer and polimer as shown in equation (5).

Cibacron red is an azo dye, it has a chemical bond N=N, degradation of the dye molecule is induced by the reaction with oxidative species (OH radicals) formed from photocatalytic process. In general, the mechanisms could be seen in Fig. 3 and 4. The OH radicals attack the azo linkage–bearing carbon (C-4) or hydroxy or amine-substituted ring. The resulting OH adduct breaks down to produce fenildiazen and phenoxy radicals. Penildiazene is extremely unstable, OH or molecule oxygen can readily oxydize it by one electron to yeld a phenidiazene radical (Fig. 3) [23]. The latter intermediate is also unstable and cleaves homolytically to generate a phenyl radical and molecular nitrogen. The phenyl might abstract a hydrogen radical to produe benzene. The oxidation of benzene into carboxylic acid, such as oxalic acid through the formation of mucondialdehyde (Fig. 4) [24]. The formation of the carboxilic acid cause the decrease in the intensity both in UV and visible area in the spectrum (Fig. 8).

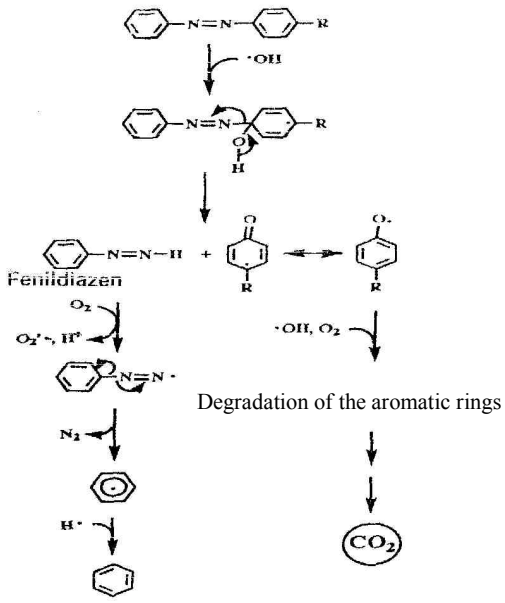

Fig. 3. The formation of benzene from azo dye [23].

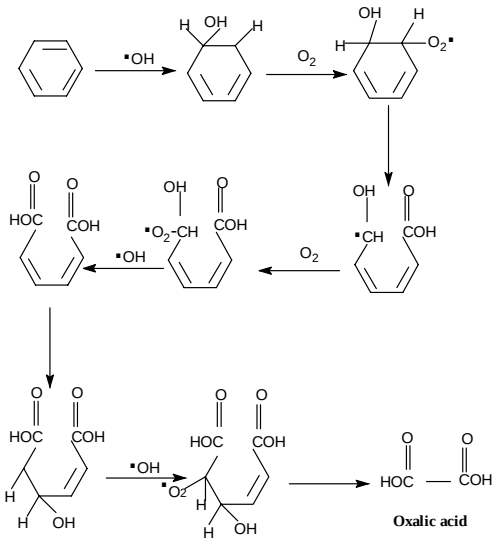

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Fig. 4 . The formation of oxalic acid from benzene [24].

Table 2. Absorbance values of cibacron red before and after six hours irradiation.

Temperature	Wave length (nm)		
	289	515	545
0	0.278	0.170	0.189
200°C	0.188	0.108	0.115
300°C	0.148	0.088	0.093
400°C	0.099	0.049	0.051
500°C	0.043	-0.007	-0.006

Table 3. The percentage of absorbance decreasing after six hours irradiation.

ZnO catalyst temperature (°C)	λ 289 nm	λ 515 nm	λ 545 nm
200	32.4 ±1.2%	39.2±0.4%	39.3±0.3%
300	46.7±0.7%	50.5±1.1%	50.7±0.7%
400	64.4±0.4%	72.5±1.4%	73.2±0.7%
500	84.5±1.0%	103.8±1.1%	102.9±0.7%

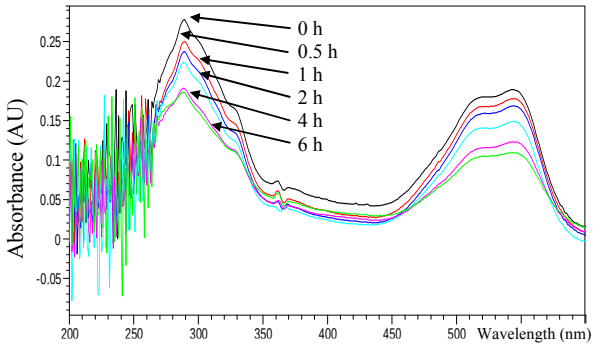

Fig. 5. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 200°C (0 h=control; 0.5 h;1 h; 2; 4 h and 6h represent hours in radiation).

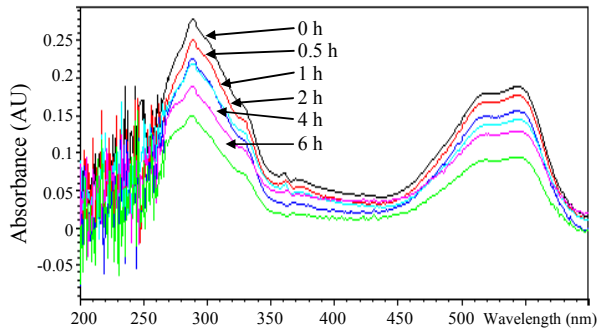

Fig. 6. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 300°C (0 h=control; 0.5 h;1 h; 2 h; 4 h and 6 h represent hours in radiation).

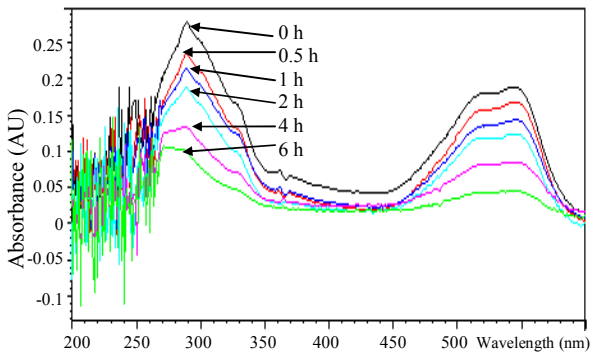

Fig. 7. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 400°C (0 h=control; 0.5 h;1 h; 2 h; 4 h and 6 h represent hours in radiation).

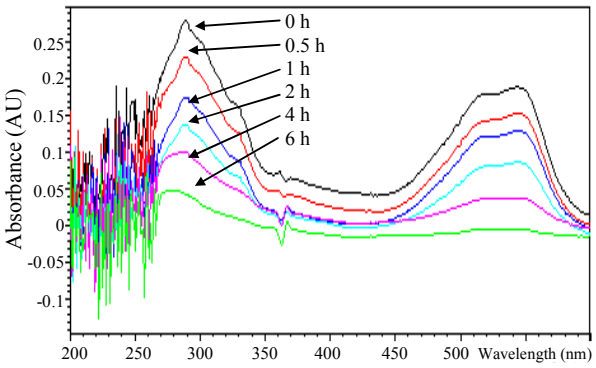

Fig. 8. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 500°C (0 h=control; 0.5 h;1 h; 2 h; 4 h and 6 h represent hours in radiation).

Reusage of ZnO catalyst

It is noted that at temperature 500°C ZnO catalyst shown a good results in degradation cibacron red solution. From this point of view, photocatalytic process using ZnO catalyst was conducted up to four times. The absorbance of cibacron red after using ZnO as a catalyst at first, second, third and fourth time are shown in Fig. 8-11, respectively. The percentage degradation of cibacron red after using catalyst several times were tabulated in Tabel 4. In the first usage the percentage degradation at 289, 515 and 545 nm were 84.5±1.0%, 100% and 100%, respectively. After second usage the percentage degradation were 64.1±2.0%, 72.8±1.1% and 75.4±0.6% at 289 nm,515 nm, and 545 nm. At the third and fourth time of the reusage of the catalyst, the efficiency decreased gradually. From the results above, it is indicated that the usage of ZnO catalyst up to four times, will significantly decrease the activity of the catalyst. Another reason suggested that the formation of the catalyst in the surface of the glass decreased already.

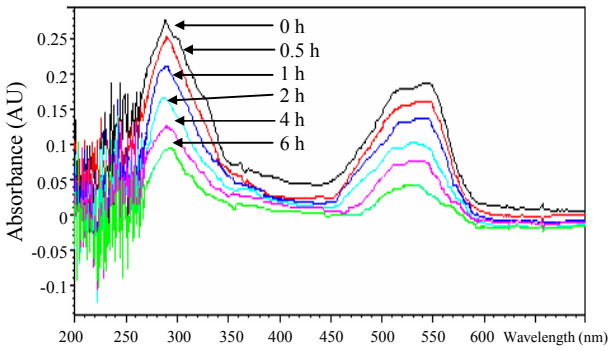

Fig. 9. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 00°C for second time (0 h=control; 0.5 h; 1 h; 2 h; 4 h and 6 h represent hours in radiation).

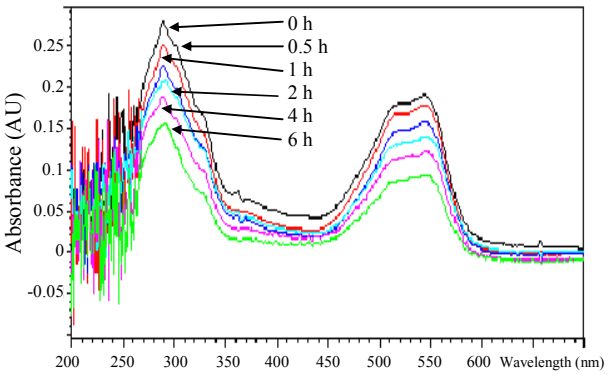

Fig. 10. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 500°C after third time (0 h=control; 0.5 h; 1 h; 2 h; 4 h and 6 h represent hours in radiation).

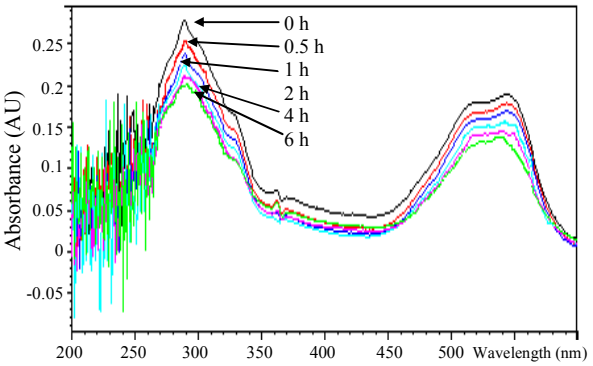

Fig. 11. Absorption spetra of cibacron red dye after photocatalytic proses using catalyst at 500°C after fourth time (0 h=control; 0.5 h; 1 h; 2 h; 4 h and 6 h represent hours in radiation).

Tabel. 4. The percentage degradation of cibacron red after reusage of ZnO catalyst

Catalyst	The percentage degradation		
	λ 289nm	λ 515nm	λ 545nm
500 °C 1st	84.5±1.0%	100%	100%
500 °C 2nd	64.1±2.0%	72.8±1.1%	75.4±0.6%
500 °C 3rd	44.2±0.09%	46.8±12%	48.4±0.6%
500 °C 4th	21.2±0.1%	23.3±0.3%	27.7±0.4%

Radiation of cibacron red at different treatment

Radiation using ZnO catalyst (500°C) was done at 6 hours at various treatment namely ie ; (a). ZnO+UV lamp, (b). ZnO without UV lamp, and (c) . UV lamp. The intensity of the spectra at 289 nm, 515 nm and 545 nm after six hours radiation with ZnO (500°C) + UV lamp decreased markedly it can

be seen from Fig. 8. The percentage degradation at 289 nm, 515 nm and 545 nm were 84.5±1.1%; 100% and 100%, respectively. The decrease in intensity is due to the destruction of the dye molecules by attack of OH radicals that formed from photocatalytic processes, the mechanisms is as follows (12) :

$$ZnO + h\nu \longrightarrow h_{vb+} + e_{cb-}$$

$$h_{vb}^{+} + H_2O \longrightarrow OH^{\bullet}$$

$$h_{vb}^{+} + OH^{-} \longrightarrow OH^{\bullet}$$

$$e_{cb}^{-} + O_2 \longrightarrow O_2^{\bullet -}$$

$$O_2\bullet- + H+ \longrightarrow HO_2\bullet$$

Figure 12 shows the treatment of cibacron red using ZnO catalyst (500°C) without UV lamp, after six hours radiation, the intensity of the spectra at 289 nm, 515 nm and 545 nm remain constant. The percentage degradation at 289nm, 515 nm and 545 nm were 5.4±1.4%, 9.1±0.7%, and 9.4±0.5%, respectively. The same phenomena also occurred when cibacron red was irradiated using UV lamp without ZnO catalyst as seen from Fig. 13. The percentage degradation at 289nm, 515 nm and 545 nm were 5.3±1.5%, 9.6±0.02%, and 9.8±0.06%, respectively

It should be mention that radiation using UV lamp without ZnO catalyst, will cause no formation of OH radicals. The OH radicals are very powerful species for degradation of the dye molecules. Therefore, degradation of cibacron red occurred effectively using ZnO catalyst (500°C) + UV lamp.

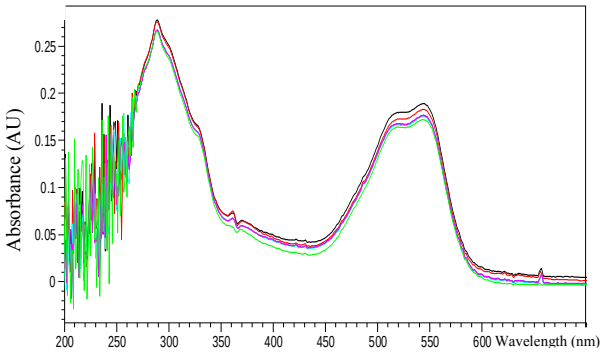

Fig. 12. Absorption spetra of cibacron red dye after treatment using ZnO catalyst (500°C).

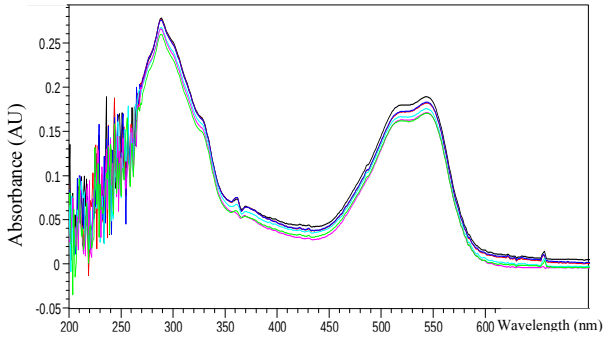

Fig. 13. Absorption spetra of cibacron red dye after treatment using UV lamp.

Table 5. shown the percentage degradation of cibacron red at various treatment namely (A). ZnO+UV lamp, (B). ZnO and (C). UV lamp. From the result it is indicated that radiation using ZnO+UV lamp resulting a good yield, due to the formation of OH radicals that can attack the structure of the dye molecules. The other two has no good resul because no formation of OH radicals.

Tabel 5. The percentage degradation of cibacron red irradiation at various treatment; (A). ZnO+UV lamp, (B). ZnO, and (C). UV lamp.

Treatment	λ 289nm	λ 515nm	λ 545nm
A	84.5±1.0%	100%	100%
B	5.4±1.4%	9.1±0.7%	9.4±0.5%
C	5.3±1.5%	9.6±0.02%	9.8±0.06%

CONCLUSION

The use of ZnO as a catalyst coated on the surface of the glass after heated at temperature 500°C could be used to degrade cibacron red dye in the photocatalytic process. The colour of the dye at 10 ppm concentration were changed after six hours radiation from red into clear colour. The degree of degradation in the 289, 515 and 545nm was achieved to be 84.5±1%%, 100% and 100%, respectively.

REFERENCES

1. W. Somasiri, R. Wenquan, X. Li and J. Chen., Electron. J. Environ. Agric. Food Chem. **5** (2006) 1.

2. N. Getoff, Rad. Phys. Chem. (2002) 437.

3. D.F. Ollis, E. Pelizzetti and N. Serpone, Environ. Sci. Tech. **25** (1991**)** 1522.

4. D.Y. Goswami, Advance Solar Energy **10** (1995) 165.
5. L.B. Reutergardh and M. Langsphasuk, Chemosphere **35** (1997) 585.
6. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, Chem. Rev. **95** (1995) 69.
7. G. Cak, F. Wypych, S.G. Moraes, N. Duran, N. Nagata and P.P. Zamora, Chemosphere **40** (2000) 433.
8. B. Dindar and S. Icli, J. Photochem. Photobiol. A **140** (2001) 261.
9. M.C. Yeber, J. Rodriguez, J. Freer, N. Duran and H.D. Mansilla, Chemosphere **41** (2000) 1193.
10. C. Lizama, J. Ferrer, J. Baeza and H.D. Mansilla, Catal. Today **76** (2002) 35.
11. K. Iketani, R.D. Sun, M. Toki, K. Hirota and O. Yamaguchi, Mater. Sci. Eng. B **108** (2004) 187.
12. J.L. Yang, S.J. An, W.I. Park, G.Y. Yi and W. Choi, Adv. Mater. **16** (2004) 1661.
13. B. Pal and M. Sharon, Mater. Chem. Phys. **76** (2002) 82.
14. F. Peng, S.H. Chen, L. Zhang, H.J. Huang and Z.Y. Xie, Acta Phys. Chem. Sin. **21** (2005) 944.
15. Y. Yamaguchi, M. Yamazaki, S. Yoshihara and T. Shirakashi, J. Electroanal. Chem. (1998) 442.
16. I. Alivov Ya, A.V. Chernykh, M.V. Chukichev and R.Y. Korotkov, Thin Solid Films **473** (2005) 241.
17. O.A. Fouad, A.A. Ismail, Z.I. Zaki and R.M. Mohamed, Appl. Catal. B **62** (2006) 144.
18. A.L. Linsebigler, L.U. Guangquan and J.T. Yates, Chem. Rev. **95** (1995) 735.
19. W. Andayani, A. Sumartono and M. Lindu, *Semiloka Nasional–Himpunan Kimia Indonesia*, Jakarta (2003).
20. A. Sumartono, W. Andayani, N. Hidayati and N.D. Utami, Prosiding Temu Jaringan Kerjasama Kimia Indonesia (2003).
21. W. Andayani, A. Sumartono and M. Lindu, Prosiding Temu Ilmiah Jaringan Kerjasama Kimia Indonesia (2002).
22. X. Feng, Zhu and H. Han, Water SA. **32** (2006) 43.
23. J.T. Spadaro, Isabelle and V.H. Renganathan, Env. Sci. Technol. **28** (1994)1389.
24. M.G. Nickelsen, W.J. Cooper, C.D. Kurucz and T.D. Waite, Environ. Sci. Technol. **26** (1992) 144.